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Disappearance of the two level spectrum for low density amorphous ice

Although the low lying excitation spectrum of two level systems (TLS) in glasses has been studied for many years with a variety of experimental techniques and theoretical models the source of these ubiquitous TLS remains outside the framework of lattice dynamics theory [1]. The surprising reports that both films of hydrogenated amorphous silicon [2] and the bulk low density phase of amorphous ice [3] do not show such TLS only reinforces the puzzling nature of these near-universal low energy excitations. The irreversible production of the high-density amorphous (HDA) phase of ice by pressure (1 – 2 GPa) at low temperatures (~77 K) makes possible the measurement of bulk amorphous samples [4]. The low density amorphous (LDA) form results from warming the HDA sample to 130 - 145 K which makes the spectroscopic investigation of the low temperature properties of both amorphous phases quite precise. Our spectroscopic study of the temperature dependent absorption of very far infrared radiation for the two forms of amorphous ice as well as its cubic and regular hexagonal crystalline phases for both H₂O and D₂O isotopes provides the framework for the discovery of this unusual spectroscopic change. Only the HDA phase, not the LDA one, shows a TLS spectrum and within the experimental uncertainties of the measurements it is independent of the H-D isotope effect. Additional spectroscopic measurements on amorphous HOD, where the local symmetry is reduced further by mixing the two kinds of hydrogen bonds, show the same TLS change between the HDA and LDA phases. This study has opened up a new high precision method for investigating the dynamical properties of the two level systems in glasses. These surprising results were presented in an invited paper at the APS March meeting in 1999.

Dependence of vibrational lifetime on the topological constraints in a glass

During the past three years we have initiated a combined persistent IR spectral hole burning and pump-probe study to examine the low temperature vibrational lifetimes of H₂ and H₂O doped into the chalcogenide glass alloy series Ge-As-Se [5]. The chalcogenide glasses are quite transparent in the IR with a window extending from about 800 cm⁻¹ to 12,000 cm⁻¹ making them ideal hosts in which to explore the dynamical properties of molecules in their electronic ground states [6]. When such glasses are doped with molecular impurities containing hydrogen or water, inhomogeneously broadened vibrational bands appear. The techniques of persistent IR spectral hole burning [7] and saturation spectroscopy [8] both have shown that the SH stretch-mode lifetime in vitreous As₂S₃ at low temperatures varies from 350 ps on the high frequency side of the absorption band to about 60 ps on the low frequency side, demonstrating a site dependent relaxation rate in which the larger the red shift of the molecular frequency, the stronger the coupling to the host. A temperature dependent study at a fixed frequency suggested that the SH stretch mode relaxes through a multi-vibrational decay into modes of the glassy host compatible with an energy gap law decay scheme. Experimentally, the mean coordination number in the Ge-As-Se alloys, which is given by $\langle r \rangle = 4X_{\text{Ge}} + 3X_{\text{As}} + 2X_{\text{Se}}$ (where X is in mole fraction), can be varied from $\langle r \rangle = 2.0$ up to values of $\langle r \rangle = 3.2$. The H₂ doped glasses have revealed a clear dependence of the hole burning [9] and refilling [10] process of the Se-H vibrational mode on the mean coordination number $\langle r \rangle$ and yield a range of lifetimes of the Se-H vibration. This result suggests that the lifetime of the mode also depends on $\langle r \rangle$. All of these findings suggest that the microscopic topology of the glass [11-14] plays a significant role in determining the vibrational mode relaxation dynamics. Since the experimental observation that the relaxation of the persistent IR hole burning spectrum could be used to distinguish chemical effects from purely topological ones needed to be tested on a short time scale, we also carried out IR picosecond pump-probe experiments on the stretch mode vibrations of H₂O in the same ternary chalcogenide glass series. Our results have confirmed that for the stretch modes the average coordination number of the glass plays the same special role in determining the short time dynamical relaxation properties as was observed for the (long time scale) persistent IR hole burning experiments [15].

Intrinsic anharmonic localized modes in crystals

An evolving idea in solid state physics is that lattice anharmonicity may make allowed localized vibrational soliton-like excitations in perfect crystals and that these localized packets of vibrational energy may move through the crystal [16,17]. Our computer simulations indicate that a natural place to look for intrinsic anharmonic localized modes in pure crystals with realistic potentials is in the gap between the optic and acoustic branches of the plane wave phonon spectrum of diatomic crystals [18-20]. Both stationary and moving anharmonic gap modes are generated in a perfect one-dimensional diatomic chain. Within the rotating-wave approximation, the eigenfrequency, eigenvector, and energy of such a localized packet can be found from differential-difference equations. For the diatomic chain the even-parity mode is unstable against conversion to an odd-parity mode and the odd-parity mode shows long-term stability in contrast with the result found earlier for a monatomic chain. Part of the mean energy of the odd-parity gap mode is

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associated with kinetic and potential terms of the ac vibration while the rest resides in a localized dc distortion of the lattice. Strongly localized gap modes can be approximated by the dynamics of a triatomic molecule. For larger vibrational amplitudes and associated dc distortions, the potential for the gap mode becomes double valued and the rotating wave approximation fails. It appears that the building blocks which we found for the development of localized modes in the one dimensional anharmonic chain can be used directly in the discussion of more complex nonlinear systems. There will be a symposium on this topic at the 1999 APS March meeting where the PI will give one of the presentations.

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13. ABSTRACT (Maximum 200 words) It has been realized for decades that spatially localized modes can occur in purely harmonic lattices only when disorder is introduced so that the translational invariance of the underlying lattice is broken. In recent years it has been noted that some vibrations in perfectly periodic lattices containing both nonlinearity and discreteness appear to localize and the study of this <i>intrinsic localization</i> in various nonlinear periodic lattices is proving quite fruitful. Recently, this earlier work has been formalized in terms of a number of useful existence and stability criteria, and many physically exciting contexts are currently emerging -- in nonlinear lattice dynamics (including fracture and friction), magnetic systems, molecular crystals, electron-phonon and magnon-phonon systems, structural biology, and nonlinear optics. The potential for these self-localized oscillatory excitations in equilibrium and nonequilibrium classical and quantum discrete lattices is now extensive and such nonlinear condensed matter research has become our major activity.					
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